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㉑ Single-stage reforming of high hydrogen content feeds for production of ammonia syn gas.

㉒ The present invention as described in Figure 2 is an improved process for the production of ammonia synthesis gas by steam reforming a desulfurized high-hydrogen content feedstock gas 122 by admixing steam 124 therewith and partially reforming the resulting gas mixture in a tubular heat exchanger 130 containing primary reforming catalyst while maintaining said gaseous mixture in indirect heat exchange with a secondary reformer effluent gas 134; recovering a partially reformed gas product 136 from the tubular heat exchanger and secondarily reforming this gas in a secondary reformer 140 in the presence of air, which is introduced to the secondary reformer in an amount sufficient to provide a hydrogen: nitrogen molar ratio of about 3:1 in the ammonia synthesis gas; and treating the reformed gas 134 in a shift conversion zone (160 + 200) to convert CO catalytically with steam to CO<sub>2</sub> and hydrogen to form a gas which can be treated for removing CO and CO<sub>2</sub> by absorption and methanation to produce the ammonia synthesis gas.

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1    SINGLE-STAGE REFORMING OF HIGH HYDROGEN CONTENT FEEDS  
1    FOR PRODUCTION OF AMMONIA SYN GAS

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2                    FIELD OF THE INVENTION

3                The present invention is directed to an improved  
4    process for the production of ammonia synthesis gas, and  
5    specifically to an improved process which utilizes a high  
6    hydrogen content feedstock gas in a single adiabatic re-  
7    forming stage without requiring a primary reforming furnace  
8    system as is conventional in present processes.

9                    DESCRIPTION OF THE PRIOR ART

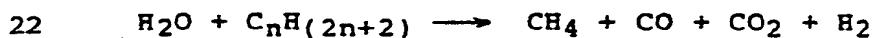
10                Generally the manufacture of ammonia consists of  
11   preparing an ammonia synthesis gas from three separate  
12   process components: a nitrogen source, usually air; steam;  
13   and a hydrogen source which is conventionally either coal,  
14   petroleum fractions, or natural gases. For example, in the  
15   preparation of ammonia synthesis gas from a light hydrocarbon  
16   feedstock, which may range from natural gas to naphtha, the  
17   hydrocarbon feedstock gas is first purified by removing  
18   gaseous contaminants, such as sulfur (which would poison the  
19   downstream catalysts) from the feedstock by the catalytic  
20   hydrogenation of the sulfur compounds to hydrogen sulfide and  
21   adsorption of the hydrogen sulfide over a zinc oxide adsorp-  
22   tion medium. Subsequent steam reforming of the contaminant-  
23   free gas provides the major portion of the hydrogen required  
24   for ammonia synthesis from the hydrocarbons in the gas.  
25   Reforming is accomplished by a two-stage process in which a  
26   mixture of steam and the purified feed gas are first reformed  
27   over catalyst in a primary reformer, followed by treatment in  
28   a secondary reformer to which air is introduced, in order to  
29   provide the required amount of N<sub>2</sub> for ammonia synthesis.  
30   However, reforming also produces carbon oxides. The carbon  
31   monoxide in the reformed gas is converted to carbon dioxide  
32   and additional hydrogen in a shift conversion step, and the  
33   carbon dioxide is removed by subsequent scrubbing. Further  
34   treatment of the raw synthesis gas by methanation is con-  
35   ventionally used to remove additional amounts of carbon

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1 dioxide and remaining carbon monoxide from the hydrogen-rich  
2 gas, resulting finally in an ammonia synthesis gas contain-  
3 ing approximately three parts of hydrogen and one part of  
4 nitrogen, that is, the 3:1 stoichiometric ratio of hydrogen  
5 to nitrogen in ammonia. The ammonia synthesis gas is then  
6 converted to ammonia by passing the gas over a catalytic  
7 surface based upon metallic iron (conventionally magnetite)  
8 which has been promoted with other metallic oxides, and  
9 allowing the ammonia to be synthesized according to the  
10 following exothermic reaction:



12 The steam reforming of the sulfur-free light hydro-  
13 carbon feedstock is conventionally carried out in a two-stage  
14 process wherein the first stage, that is primary reforming,  
15 produces a partially reformed gas. This partially reformed  
16 gas is introduced along with air into a second stage, that is  
17 secondary reforming, to obtain a greater concentration of  
18 hydrogen and a lesser concentration of hydrocarbons. The  
19 reaction processes occurring in the reforming of the feed-  
20 stock gas begin with the breakdown of hydrocarbons to  
21 methane, carbon dioxide and carbon monoxide:



23 and end with the reforming of these products by the desired  
24 endothermic methane reforming reaction:



26 and by accompanying exothermic reactions:



31 The methane reforming reaction for the production of  
32 hydrogen is highly endothermic and, for feedstocks containing  
33 less than about 80 vol.% H<sub>2</sub> a large heat transfer is  
34 required, which conventionally involves the use of a high  
35 capital investment primary reforming furnace, which also  
36 consumes a significant amount of energy in the form of fuel.  
37 The catalyst for this primary reforming is normally a nickel  
38 catalyst supported on alumina.

1        The subsequent secondary reforming step takes place in  
2 a refractory-lined vessel which also contains a nickel  
3 catalyst supported on alumina. In conventional steam  
4 reforming processes, air is introduced into this adiabatic  
5 reforming stage to provide the needed nitrogen for the  
6 production of ammonia synthesis gas. Oxygen in the air also  
7 reacts with the combustion components in the gas stream  
8 coming from the primary reforming stage to increase the  
9 temperature and provide heat for this additional reforming of  
10 hydrocarbons.

11       U.S. Patent 3,442,613 discloses a two-stage reforming  
12 process in which milder primary reforming conditions are  
13 employed which results in a larger amount of methane in the  
14 primary reformer effluent. Excess air is then fed to the  
15 secondary reformer to permit increased exothermic hydrogen  
16 combustion therein, which aids in the reforming of the larger  
17 methane volumes fed thereto. Thereafter, the excess N<sub>2</sub>,  
18 introduced via the air feed to the secondary reformer, is  
19 removed in a cryogenic separation step.

20       U.S. Patent 3,584,998 relates to a one-stage reforming  
21 process in which natural gas, excess air and steam are  
22 preheated in heat exchange with reformer effluent gas and  
23 then reformed, followed by water gas shift and CO<sub>2</sub> scrubbing  
24 treatments and then by a cryogenic process in which excess N<sub>2</sub>  
25 is removed from the scrubbed reformer effluent gas.

26       U.S. Patent 3,649,558 also relates to a single stage  
27 reformer, in which air is introduced in excess amounts to the  
28 secondary-type reformer. Excess N<sub>2</sub> is removed in a subsequent  
29 cryogenic section.

30       U.S. Patents 4,079,017 and 4,162,290 relate to the use  
31 of parallel steam reformers for the primary reforming of the  
32 hydrocarbon feed.

33       B. Chatterjee, "Ammonia From Hydrocarbons--An Improved  
34 Process", Fertiliser News, pp. 19-22 (December 1980) dis-  
35 closes another single-stage reforming process in which  
36 oxygen-enriched excess air is combined with natural gas and  
37 steam and reacted in an autothermal reformer, followed by  
38 shift reactions, boiler feed water heat recovery, CO<sub>2</sub>

1 recovery and methanation. Excess methane remains in the  
2 reformer effluent gas and is removed in a downstream cryo-  
3 genic section, which also serves to separate excess N<sub>2</sub>.  
4

5 SUMMARY OF THE INVENTION

6 The present invention, is broadly directed to an  
7 improved process for the production of ammonia synthesis gas,  
8 and specifically to an improved process which utilizes a  
9 high-hydrogen content feedstock gas in a single adiabatic  
10 reforming stage without requiring a primary reforming furnace  
11 system as is conventional in present processes.

12 The improved process of this invention provides an  
13 ammonia synthesis gas which, after shift conversion, is  
14 characterized by low methane content and does not contain  
15 excess nitrogen, and which can therefore be passed directly,  
16 after conventional treatment for CO<sub>2</sub> scrubbing and methan-  
17 ation, to an ammonia synthesis reactor for formation of  
18 ammonia. The process therefore produces an ammonia syn gas  
19 stream without the need for use of the expensive cryogenic  
20 purification processes required by the prior art, and at the  
21 same time avoids the need to use a conventional primary  
22 reformer. This results in a large savings in equipment costs  
23 and on-going operating expenses.

24 The process of this invention also permits the use of  
25 higher process pressures in the reforming section than have  
26 heretofore been possible due to pressure design limitations  
27 imposed by current primary reformer tubing metallurgy.

28 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of a two-stage  
30 primary/secondary reforming process of the prior art.

31 Figures 2 and 3 are a schematic illustration of one  
32 embodiment of the process of the present invention.

33 Figure 4 is a schematic illustration of a  
34 reactor/exchanger for use in a second embodiment of the  
35 process of this invention.

36 DETAILED DESCRIPTION OF THE INVENTION

37 Referring to the drawings, and specifically the

1 conventional primary and secondary reforming stages which  
2 have been highly simplified and illustrated in Figure 1,  
3 there is seen a primary reforming furnace stage generally  
4 indicated by the numeral 10, having an upper convection  
5 section 8, and a lower primary reforming radiant section 12.  
6 The furnace is normally heated by burners mounted in the  
7 floor of the radiant section and supplied with fuel gas and  
8 combustion air as illustrated. Hot flue gas exiting the  
9 radiant section flows upwardly through convection section 8,  
10 past steam superheat exchangers 4 and 6, process air heat  
11 exchanger 7, steam generators 9 and 11, steam superheat  
12 generator 13, feed gas heat exchangers 15, and 16 and  
13 boiler feed water preheater 17, and is discharged through  
14 port 3.

16 As discussed previously, conventional two-stage  
17 reforming processes require the introduction of four separate  
18 process streams to the primary reformer: feed gas (for a  
19 source of hydrogen), steam, a source of nitrogen gas (which  
20 is conventionally process air) and fuel gas. Feed gas is  
21 introduced into the process and passes through feed gas heat  
22 exchangers 16 and 15, positioned in the primary reforming  
23 furnace's convection section 8.

24 This preheats the feed gas to approximately 750°F, the  
25 required temperature for the removal of sulfur over a zinc  
26 oxide desulfurization bed 20. Steam is produced by passing  
27 boiler feed water through heat exchangers 17, 9, and 11, and  
28 by passing the resulting steam for superheating through  
29 exchangers 13, 6 and 4, via steam drum 18, as shown, to  
30 achieve a steam temperature of approximately 1200°F. This  
31 steam is then combined with the desulfurized feed gas and fed  
32 to catalyst-filled reformer tubes 14 in radiant section 12.  
33 The partially reformed feed gas 28 is then discharged from  
34 the primary reformer furnace and fed into secondary adiabatic  
35 reformer 30 where it is combined with process air 29 that has  
36 been preheated in heat exchanger 7 to about 1200°F. The  
37 oxygen in this preheated process air reacts with combustibles  
38 (H<sub>2</sub>, CO, and CH<sub>4</sub>) in the partially reformed feed gas, and  
39 releases additional heat. Upon entering the secondary

1 reformer's catalyst bed the gas mixture undergoes additional  
2 reforming with a decrease in temperature due to the more  
3 predominant endothermic reaction. The raw synthesis gas is  
4 discharged from the secondary reformer and undergoes addi-  
5 tional processing in conventional steps: carbon dioxide is  
6 formed from carbon monoxide in shift converter unit 40;  
7 carbon dioxide is removed in process unit 50; carbon monoxide  
8 and additional carbon dioxide is removed by methanation in  
9 process unit 60; the synthesis gas is compressed in com-  
10 pressor 70 to that required for ammonia synthesis in the  
11 ammonia synthesis system 80; vaporous ammonia undergoes  
12 further compression in refrigeration compressor 90; and is  
13 withdrawn from the process as ammonia product. Excess heat in  
14 the ammonia synthesis section is removed by means of boiler  
15 feed water heat exchanger 82.

16 Referring to Figure 2, wherein one embodiment of the  
17 process of this invention is illustrated, the selected  
18 high-hydrogen content feedstock is passed via conduit 108 to  
19 first heat exchanger 110 wherein it is heated, generally to a  
20 temperature of from about 300 to 350°F, by indirect heat  
21 exchange with a low temperature shift converter effluent gas,  
22 to be described in more detail below, which is passed to  
23 exchanger 110 via conduit 201.

24 The gas feedstocks which can be treated in accordance  
25 with the process of this invention for single-stage reforming  
26 are gases containing high concentrations of hydrogen, i.e.,  
27 hydrogen concentrations greater than about 40 vol.%, and  
28 preferably greater than about 50 vol.% H<sub>2</sub>, and most typically  
29 from about 50 to 80 vol.% H<sub>2</sub>, in addition to lower hydro-  
30 carbons, small concentrations of carbon monoxide, and trace  
31 gases, such as CO<sub>2</sub>, H<sub>2</sub>S, COS, N<sub>2</sub> and argon. The lower  
32 hydrocarbons present in the gas feed generally comprise  
33 members selected from the group consisting of saturated  
34 aliphatic hydrocarbons having from 1 to 4 carbon atoms, and  
35 unsaturated aliphatic hydrocarbons having from 2 to 4 carbon  
36 atoms; are principally methane but also inclusive of  
37 ethylene, ethane and the like; and are generally present in a  
38 concentration of from about 15 to 30 vol.%. The carbon

1 monoxide concentration in the gas feed is not critical and  
2 will generally range from about 0 to 25 vol.%. Among these  
3 potential high-hydrogen content feedstocks are coke gas or  
4 refinery gases, such as are discussed in U.S. Patent  
5 3,649,558, in addition to coal pyrolysis gas, and feedstocks  
6 such as those available from an intermediate BTU gas (IBG)  
7 streams resulting from the gasification of coal or lignite  
8 using conventional gasification processes.

9 The heated feed gas is withdrawn from exchanger 110 via  
10 conduit 112 and may be admixed with sufficient steam (which  
11 can be introduced to conduit 112 via conduit 111) to supply  
12 the water of reaction required for a subsequent COS hydroly-  
13 sis reaction (which can be effected in COS hydrolysis reactor  
14 114), if COS is present in the feed. The quantity of steam  
15 which is thus introduced can vary widely and will generally  
16 comprise from about 2 to 4 vol.%, based on the total feed  
17 gas in conduit 112 withdrawn from exchanger 110. The COS  
18 reaction in reactor 114 can be effected by any conventional  
19 means, using conventional hydrolysis catalysts such as  
20 activated alumina. In this reactor, COS contained in the feed  
21 gas is converted into hydrogen sulfide gas at conventional  
22 hydrolysis conditions, which typically range from about 300  
23 to 350°F and from about 300 to 600 psig. If the feedstock  
24 gas does not contain COS, steam injection line 111 and COS  
25 hydrolysis reactor 114 can be eliminated from the system if  
26 desired.

27 The resulting gas mixture is withdrawn via conduit  
28 116 and is introduced into second heat exchanger 118 wherein  
29 the gas is further heated, in this case by indirect heat  
30 exchange with a high temperature shift converter gas effluent  
31 (to be described in more detail below), which is introduced  
32 thereto via conduit 164. Thereafter, the further-heated gas  
33 which may contain the hydrogen sulfide and which will  
34 generally have a temperature of from about 700 to 750°F, is  
35 withdrawn via conduit 117 and introduced into sulfur removal  
36 zone 120, wherein the hydrogen sulfide impurities are removed  
37 from the gas stream by conventional technology, such as by  
38 use of a zinc oxide adsorption bed. The gas, now essentially

1 free of sulfur impurities (e.g., containing less than about  
2 0.2 ppm by weight of sulfur compounds, calculated as elemen-  
3 tal sulfur), is withdrawn via conduit 122 and admixed with  
4 steam, which can be accomplished by injected steam into  
5 conduit 122 via conduit 124. Again, the quantity of steam  
6 introduced at this point can vary, and will generally range  
7 from about 2.5 to 4.0 moles per mole of carbon in the  
8 desulfurized gas feed. The function of the steam introduced  
9 at this point in the process is to provide the water of  
10 reaction necessary for the subsequent reforming reactions.  
11 The steam/desulfurized gas mixture is then further heated  
12 (generally to a temperature of from about 800 to 1,000°F) in  
13 third heat exchanger 126 by indirect heat exchanger with a  
14 portion of the reactor/exchanger effluent gas (to be des-  
15 cribed in more detail below) which is introduced to exchanger  
16 126 via conduit 138. The thus-heated steam/desulfurized gas  
17 mixture 128 is introduced into the tube side of tubular heat  
18 exchanger 130 wherein the feed gas is at least partially  
19 reformed by contacting the feed gas, under reforming condi-  
20 tions, in tubes 121 of reactor/exchanger 130 with a conven-  
21 tional reforming catalyst. Any conventional primary  
22 reforming catalyst can be employed, such as nickel, nickel  
23 oxide, chromia, molybdenum, mixtures thereof and the like,  
24 with nickel-on-calcium aluminate or nickel-on-alumina being  
25 preferred. The temperature within tubes 121 will generally  
26 range from about 900 to 1500°F and the pressure will gener-  
27 ally range from about 300 to 1000 psig, and the total gas  
28 hourly space velocity in tubes 121 will generally range from  
29 about 5000 to 15,000 v/v/hr., with a range of from 8000 to  
30 10,000 v/v/hr. being preferred.

31 As a result of the reforming reactions occurring in  
32 tubular exchanger 130, substantially all of the hydrocarbon  
33 components of the feed gas (other than methane) are converted  
34 to CH<sub>4</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>; a portion of the original methane  
35 components are likewise converted to CO, CO<sub>2</sub> and H<sub>2</sub>; and the  
36 temperature of the gas mixture will be generally increased to  
37 about 1300 to 1450°F. The partially reformed gas will

1 generally have a residual methane level of from about 5 to  
2 20 vol.% CH<sub>4</sub>, on a dry basis.

3       Process air obtained from any convenient source is  
4 passed via conduit 197 to fourth heat exchanger 196 wherein  
5 it is heated (generally to a temperature of from about 700 to  
6 800°F) by indirect heat exchange with a portion of the high  
7 temperature shift converter effluent gas which is passed  
8 thereto via conduit 166. The thus-heated process air is  
9 withdrawn via conduit 195 and passed to yet another heat  
10 exchanger 194 for further heating (generally to a temperature  
11 of from about 900 to 1000°F) by indirect heat exchange with a  
12 portion of the cooled reformer effluent gas, which is passed  
13 thereto via conduit 135 from the shell side of exchanger 130.  
14 The thus-heated process air is then introduced via conduit  
15 141 into secondary reformer 140, together with the partially  
16 reformed gas mixture which is introduced via conduit 136.

17       The quantity of air introduced via conduit 141 is  
18 adjusted using conventional control means (not shown), to  
19 provide an air:feed ratio sufficient to yield about a 3:1  
20 hydrogen:nitrogen ratio in the ammonia synthesis gas, that  
21 is, to provide a H<sub>2</sub>:N<sub>2</sub> ratio of from about 2.6:1 to 3.2:1,  
22 and preferably from about 2.8:1 to 3.1:1.

23       Secondary reformer 140 comprises an adiabatic reformer  
24 of conventional design and can be provided with suitable  
25 internal burners to be used during start-up of the process in  
26 order to bring the temperature within the reformer to within  
27 the range of from about 1400 to 1600°F, after which further  
28 heating can be accomplished via the heat released in the  
29 exothermic reaction of oxygen therein with feedstock. The  
30 amount and type of catalyst in reformer 140 is also con-  
31 ventional, with Ni catalysts supported on alumina being  
32 typical. The secondary reformer will generally employ a  
33 temperature of from about 1600 to 1900°F, a pressure of from  
34 about 300 to 1000 psig, and a total gas hourly space velocity  
35 of from about 7000 to 10,000 v/v/hr.

36       The reformer effluent gas (generally having a tem-  
37 perature of from about 1600 to 1800°F and a residual CH<sub>4</sub>  
38 level of from about 0.2 to 0.6 vol.% CH<sub>4</sub>, on a dry basis) is

1 withdrawn from secondary reformer 140 via conduit 134 and is  
2 passed to the shell side of reactor/exchanger 130 for  
3 indirect heat exchange with, and heating of, the  
4 steam/desulfurized feed gas mixture passed to exchanger 130  
5 via conduit 128, as described above. The effluent gas  
5 withdrawn via conduit 132 is then divided into two portions.  
7 A first portion is passed via conduit 138 to third heat  
8 exchanger 126 for indirect heat exchange with, and heating  
9 of, the steam/desulfurized gas mixture as described above.  
10 The second portion is passed via conduit 135 to fifth  
11 exchanger 194 to provide the final stage of heating of the  
12 process air in conduit 195 prior to its injection into  
13 secondary reformer 140. The partially cooled reformer  
14 effluent gas is withdrawn from third exchanger 126 via  
15 conduit 139 and passed to steam superheater 142 and first  
16 steam generator 158, superheater 142 receiving steam via  
17 conduit 144 (generally at a temperature of from about 590 to  
18 600°F and about 1500 psig) from steam drum 150 and producing  
19 superheated steam which is withdrawn via conduit 143  
20 (generally at a temperature of about 800 to 900°F and about  
21 1500 psig), and generator 158 in turn generating steam 159  
22 from water stream 157 which is fed thereto from steam drum  
23 150. From generator 158, the cooled reformer effluent is  
24 passed via conduit 155 to high temperature shift converter  
25 160, wherein carbon monoxide in the reformer effluent gas is  
26 converted over conventional catalysts and using conventional  
27 methods and equipment to carbon dioxide and additional  
28 hydrogen. Partially cooled effluent gas is also withdrawn  
29 via conduit 137 from fifth exchanger 194 and is recombined  
30 with the remaining reformer effluent in conduit 155.

31 Generally, a temperature of from about 700 to 900°F and  
32 a pressure of from about 300 to 1000 psig will be employed in  
33 converter 160, and the catalyst will generally comprise a  
34 supported, chromium-promoted iron catalyst. Thereafter, gas  
35 exiting the high temperature shift converter is withdrawn via  
36 conduit 162 and is itself split into two portions. A first  
37 portion is passed via conduit 164 to second heat exchanger  
38 118 for heating of the gas feed to desulfurization zone 120,

- 11 -

1 as described above. The partially cooled effluent gas is  
2 then withdrawn via conduit 165 from exchanger 118 and passed  
3 to low temperature shift converter 200, preferably after  
4 treatment in guard bed 190.

5 The second portion of the gaseous effluent from the  
6 high temperature shift converter 160 is passed via conduit  
7 169 to a second steam generator 152 in which steam 151 is  
8 produced from water feed 153 and is returned to drum 150 from  
9 which water 153 was received. The partially cooled high  
10 temperature shift effluent from generator 152 is then itself  
11 split into two portions: a first part is passed via conduit  
12 166 to fourth heat exchanger 196 to provide the first stage  
13 of heating of the process air, introduced thereto via conduit  
14 197, as described above. The further cooled effluent gas is  
15 then withdrawn via conduit 167 and passed to conduit 165 for  
16 combined feed to the low temperature shift converter 200, or  
17 preferably first to guard bed 190.

18 The second part of shift effluent from exchanger 152 is  
19 passed via conduit 168 to boiler feedwater exchanger 170 in  
20 which boiler feedwater, introduced thereto via conduit 180,  
21 is heated and from which the further cooled shift effluent is  
22 withdrawn (via conduit 174) and combined with stream 165 for  
23 feed to low temperature shift converter 200, or preferably  
24 first to guard bed 190. If desired, feedwater 180 can be  
25 first heated by exchange with low temperature shift effluent  
26 201 in a separate exchanger (not shown) prior to introduction  
27 to exchanger 170.

28 Guard bed 190, which is optional, is preferably  
29 employed to treat gas stream 165 upstream of low temperature  
30 shift converter 200 to remove halide and sulfur impurities  
31 and thereby protect any halide- and sulfur-sensitive catalyst  
32 in low temperature shift converter 200. The operation of  
33 guard bed 190 is conventional and is generally conducted at  
34 temperatures and pressures within the ranges used in low  
35 temperature shift converter 200 as described below, and the  
36 solids employed in guard bed 190 for such halide- and  
37 S-impurities removal generally comprise the same catalyst as  
38 is used in low temperature shift converter 200.

1        In shift converter 200, a low temperature shift  
2 conversion reaction is effected over conventional catalyst  
3 using conventional methods and equipment to form additional  
4 quantities of H<sub>2</sub> and CO<sub>2</sub>. Generally, a temperature of from  
5 about 400 to 500°F and a pressure of from about 300 to 1000  
6 psig will be employed in converter 200, and the catalyst will  
7 generally comprise a mixture of zinc oxide and copper. The  
8 effluent gas from low temperature shift converter 200 is  
9 passed via conduit 201 to first heat exchanger 110, as  
10 described above, for heating of the feed gas introduced  
11 thereto via conduit 108. The cooled, low temperature shift  
12 converter effluent gas, now depleted of its heat values, is  
13 then withdrawn via conduit 106 and (referring now to Figure  
14 3) can be passed to CO<sub>2</sub>-removal zone 250, in which any  
15 conventional process (e.g., solvent absorption of CO<sub>2</sub> gas)  
16 can be used to remove CO<sub>2</sub> via conduit 210. The resulting  
17 CO<sub>2</sub>-free gas is fed by conduit 220 to conventional methana-  
18 tor zone 300 for removal of additional CO and CO<sub>2</sub> and is then  
19 withdrawn (via conduit 320), compressed in compressor 350 and  
20 passed as direct feed via conduit 370 to ammonia synthesis  
21 zone 400, wherein NH<sub>3</sub> is formed from the H<sub>2</sub>/N<sub>2</sub> synthe-  
22 sis gas 370 (i.e., 3:1 H<sub>2</sub>:N<sub>2</sub> molar ratio) using conven-  
23 tional techniques (i.e., over Fe-catalyst at 700 to 950°F).  
24 Waste gases are withdrawn via conduit 410 and product NH<sub>3</sub> is  
25 recovered via conduit 420.

26        The operation of CO<sub>2</sub> removal zone 250, methanation zone  
27 300, compressor 350 and NH<sub>3</sub> synthesis zone 400 is conven-  
28 tional and need not be more completely described for a full  
29 understanding of the process of this invention. The precise  
30 operating parameters and equipment of each such process step,  
31 therefore, will be readily apparent to one having ordinary  
32 skill in the art, and each step can include the usual  
33 internal recycle streams and stages found useful in the prior  
34 art. Thus, CO<sub>2</sub>-removal zone 250 can include conventional  
35 CO<sub>2</sub>-absorption and CO<sub>2</sub>-desorption stages wherein the  
36 CO<sub>2</sub>-laden gas 106 is contacted with a liquid containing  
37 either a solvent for, or a dissolved compound (e.g., K<sub>2</sub>CO<sub>3</sub>)  
38 readily reactive with, the CO<sub>2</sub>; the CO<sub>2</sub>-free gases (generally

1 containing less than about 0.15 vol.% CO<sub>2</sub>) are withdrawn; and  
2 the solvent is treated to desorb the CO<sub>2</sub> gases 210 for  
3 recycle of solvent to the absorber. Exemplary of suitable  
4 conventional CO<sub>2</sub> removal systems are those discussed in  
5 Kirk-Othmer, Encyclopedia of Chemical Technology, 3d Ed.,  
6 Vol. 2, pp. 492-494 (1978). Similarly, methanator 300 will  
7 generally employ a temperature in the range of about 570 to  
8 940°F, a pressure from about 300 to 1000 psig, and a sup-  
9 ported Ni catalyst (e.g., Ni on alumina) to convert any  
10 remaining CO and CO<sub>2</sub> in gas stream 220 to methane, thereby  
11 producing an effluent gas 320 containing less than about 10  
12 vppm (i.e., parts per million by volume) of total CO and CO<sub>2</sub>  
13 and H<sub>2</sub> and N<sub>2</sub> in a H<sub>2</sub>:N<sub>2</sub> molar ratio of from about 2.6:1 to  
14 3.1:1. Compression in zone 350 can take place in several  
15 stages, as desired, to bring the methanator effluent to  
16 synthesis reactor pressure, which generally ranges from about  
17 2000 to 5000 psig. Finally, ammonia synthesis zone 400 can  
18 include conventional dryer units wherein trace water is  
19 removed from the syn gas as required and conventional purge  
20 recovery units wherein a portion or all of the gas effluent  
21 from the ammonia synthesis reactor is treated to recover and  
22 recycle H<sub>2</sub> to the reactor and to remove inerts such as CH<sub>4</sub>  
23 and Ar therefrom.

24 The improved process of this invention produces a syn  
25 gas 370, having a H<sub>2</sub>:N<sub>2</sub> molar ratio of about 3:1, that is a  
26 H<sub>2</sub>:N<sub>2</sub> molar ratio of from about 2.6:1 to 3.2:1, and which has  
27 a residual methane concentration (dry basis) of less than  
28 about 2 vol.%, and more typically less than about 1 vol.% and  
29 which is therefore suitable for direct feed to an ammonia  
30 synthesis reactor zone 400, that is a syn gas 320 which is  
31 not subjected to a cryogenic purification following methana-  
32 tor 300 to remove excess methane prior to the ammonia  
33 synthesis reaction. The elimination of the cryogenic section  
34 required by the prior art and the avoidance of the use of a  
35 primary reformer furnace by the improved process of this  
36 invention results in a very large savings in terms of  
37 equipment investment and operating expense.

38 In accordance with another embodiment of the process of  
39 this invention, illustrated in Figure 4, steam/desulfurized

1 gas mixture 128a is passed to the shell side of reactor/  
2 exchanger 130a and the selected reforming catalyst is  
3 housed in the shell side of apparatus 130a. The steam/  
4 desulfurized gas mixture is at least partially reformed  
5 over the catalyst while being heated by means of reformer  
6 effluent gas 134a, which in this embodiment is passed to the  
7 tube side 121a of reactor/exchanger 130a. The partially  
8 reformed gas 136a and the partially cooled reformer effluent  
9 gas 132a are withdrawn and further treated as described above  
10 for streams 132 and 136, respectively, in the embodiment  
11 illustrated in Figure 2. The conditions of operation of  
12 apparatus 130a in Figure 4 correspond to those discussed  
13 above for apparatus 130 in the embodiment illustrated in  
14 Figure 2.

15 To further illustrate the process, a feed gas con-  
16 taining 52 vol.% H<sub>2</sub>, 20 vol.% CO, 28 vol.% CH<sub>4</sub> and 30 vppm  
17 COS, having a temperature of about 110°F and a pressure of  
18 about 350 psig, is preheated to about 315°F in tubular feed  
19 gas preheat exchanger 110, and is then introduced into COS  
20 hydrolysis drum 114, after addition of 2 vol.% steam (750°F,  
21 600 psig), based on total feed gas 112, (withdrawn from  
22 exchanger 110), in which the carbonyl sulfide is converted to  
23 hydrogen sulfide over a bed of an alumina hydrolysis catalyst  
24 (at 315°F, 350 psig, 2000 v/v/hr. gas hourly space velocity).  
25 The temperature of the resulting feed gas is increased to  
26 about 750°F, the temperature required for further desulfur-  
27 ization, by passing the hydrogen-sulfide-containing gas  
28 through tubular heat exchanger 118, followed by adsorption of  
29 the hydrogen sulfide over a zinc oxide adsorption bed 120.

30 To the sulfur-free feed gas discharged from zinc oxide  
31 adsorption bed 120 is then added 3.0 moles of steam (750°F,  
32 600 psig) per mole of carbon in the feed gas, and this  
33 combined stream passes through tubular heat exchanger 126 in  
34 order to increase the gas temperature to about 900°F.

35 An additional increase in the temperature of this  
36 combined stream (to about 1400°F) is obtained by subsequent  
37 preheat treatment in the tube side 121 of reactor/exchanger  
38 130 in indirect heat exchange with reformer effluent gas

1 entering the shell side of exchanger 130 and in contact with  
2 nickel on alumina reforming catalyst in tubes 121 (at 1375°F,  
3 325 psig, 9000 v/v/hr.) so that partial steam reforming of  
4 hydrocarbons takes place in exchanger 130, further con-  
5 tributing to the preheat of this feed stream to be charged to  
6 reformer 140.

7 Process air is adjusted using conventional control  
8 means (not shown) to provide an air:feed ratio sufficient to  
9 yield about a 3:1 H<sub>2</sub>:N<sub>2</sub> ratio in the final product ammonia  
10 synthesis gas 320. The adjusted process air enters the  
11 process by first being pressurized (compressor not shown) to  
12 about 50 psi above the pressure used in reformer 140. The  
13 pressurized process air is then preheated in tubular heat  
14 exchangers 196 and 194 to a reforming inlet temperature of  
15 about 1000°F.

16 The heated process air feed and the steam-feed gas  
17 streams are then introduced into adiabatic reformer 140  
18 wherein reforming of the feed gas takes place over Ni on  
19 alumina reforming catalyst (at a space velocity of about 7000  
20 v/v/hr.).

21 The reformer effluent gas from reformer 140 (1730°F,  
22 320 psig) is discharged, as discussed above, into the shell  
23 side of exchanger 130, and from exchanger 130 (1130°F, 315  
24 psig) is passed to feed preheat exchanger 126 and air preheat  
25 exchanger 194. The partially cooled reformer effluent from  
26 feed gas preheat exchanger 126 is passed to steam superheater  
27 142 and first steam generator 158 for generation of 1500 psig  
28 steam, and the resulting cooled reformer effluent withdrawn  
29 from generator 158 is combined with the remaining cooled  
30 reformer effluent 137 and passed via conduit 155 (700°F, 310  
31 psig) to high temperature shift converter 160. In converter  
32 160, a water gas shift reaction is effected over an  
33 iron-based catalyst (720°F inlet temperature, 310 psig) to  
34 form H<sub>2</sub> and CO<sub>2</sub> from CO contained in the reformer effluent  
35 gas. Gases exiting converter 160 (850°F, 300 psig) are then  
36 passed to heat exchangers 118, 196 and 170 and steam  
37 generator 152 (generating steam at 1500 psig) as described  
38 above, combined in conduit 165 (420°F, 300 psig) and fed to

1 low temperature converter guard bed 190 containing ZnO/Cu  
2 solids to absorb any Cl and S values which may be present,  
3 followed by treatment in low temperature shift converter 200  
4 containing conventional ZnO/Cu shift conversion catalyst.  
5 After passing through heat exchanger 110, the product gases  
6 (at 450°F, 290 psig) are withdrawn via conduit 106, and  
7 treated for CO<sub>2</sub> removal in CO<sub>2</sub> removal zone 250, methanated  
8 in methanator 300, compressed and then fed to ammonia  
9 synthesis zone 400, as described above. The ammonia synthesis  
10 gas withdrawn from methanator 300 contains H<sub>2</sub>:N<sub>2</sub> in about a  
11 3:1 molar ratio and contains less than about 1.0 vol.% CH<sub>4</sub>  
12 (dry basis), and less than about 10 vppm CO and CO<sub>2</sub>.

13 A feedstock 108 suitable for the single stage reforming  
14 process of the present invention is, for example, a steam  
15 cracker tail gas having a hydrogen content of about 70%, with  
16 the remainder being methane, or an IBG stream from a coal  
17 gasification process having major component composition of  
18 hydrogen (60%), carbon monoxide (20%), and methane(16%).

19 Still another feedstock suitable for the single stage  
20 reforming process of the present invention, and that used as  
21 the feedstock material for obtaining the data in Table 1 has  
22 the composition of hydrogen (52.13%), carbon monoxide  
23 (19.39%), methane (27.03%), carbon dioxide (0%), nitrogen  
24 (0%), and mixed 2-carbon hydrocarbons (1.45%).

25 A comparison of the parameters is tabulated in the  
26 following Table 1 for (1) a conventional process as shown in  
27 Figure 1, except that the primary reformer is omitted,  
28 conducted at the maximum practical preheat temperature for  
29 feedstock and air; and (2) single stage reforming using the  
30 feed/effluent reactor/exchanger 130, as depicted in Figure  
31 2.

TABLE 1  
SIMPLE-STAGE REFORMING OF  
IBG FOR AMMONIA SYNTHESIS GAS

Maximum Feed Preheat-Conventional (without Primary Reforming)	Apparatus/Stream No. (Fig. 1*) (1)	Reactor/ Exchanger (Figures 2&3)	Apparatus/Stream No. (Figures 2&3)
Feed/Steam Preheat Temperature, °F	916	28	900
Air Preheat Temperature, °F	1000	29	1000
Steam/Feed, mol/mol	1.479	28	1.479
Reformer Pressure, psia	350	30	335
Vol. % O <sub>2</sub> in Air Stream	20.95	29	20.95
Reformer Feed/Steam Inlet Temperature, °F	916	28	1375
Reformer Outlet Temperature, °F	1413	32	1732
Vol. % CH <sub>4</sub> in Reformer Outlet (dry basis)	5.86	32	0.34
Vol. % CH <sub>4</sub> in Syn Gas Product (dry basis)	7.04	66	0.92
Feed Gas/Product H <sub>2</sub> , mol/mol	0.88	66	0.65
		320	

1 Figure 1\* = process of figure 1 without reforming in primary reformer 10: composition of feed gas/steam mixture 24 is the same as stream 28 which is passed directly to secondary reformer 30.

1       Table 1 clearly indicates that a feed/steam preheat to  
2 1375°F in the reactor/exchanger and accompanying partial  
3 reforming of hydrocarbons therein results in a decrease in a  
4 final product syn gas methane content from an unacceptably  
5 high 5.86 vol.% to 0.34 vol.%, thereby indicating the greatest  
6 reforming efficiency obtained utilizing the reactor/exchanger  
7 130.

8       When the amount of feed gas required to produce a  
9 constant amount of hydrogen in the ammonia syn gas is  
10 calculated, the efficiency of the total process is easily  
11 seen. For example, as shown in Table 1, 0.65 lb-mols/hr. of  
12 feed gas are required to produce 1.0 lb-mols/hr. of hydrogen  
13 in the product syn gas in the reactor/exchanger process  
14 design depicted in Figure 2, whereas 0.88 lb-mols/hr. of feed  
15 gas are required to produce the same amount of hydrogen under  
16 the conventional process design depicted in Figure 1 when the  
17 primary reformer is omitted.

18       The advantages of the process design according to the  
19 present invention are therefore seen as a reduction in  
20 capital expenditure associated with the construction of a  
21 primary reforming furnace, as otherwise required to produce  
22 an acceptable concentration of methane in product synthesis  
23 gas, an economic savings in utility costs expended in the  
24 heating of said primary reforming furnace, a desirable  
25 decrease in the methane slippage of the ammonia syn gas  
26 produced, and a greater efficiency in utilizing the feed gas  
27 requirements to yield the ammonia syn gas produced.

28       Thus, while I have illustrated and described the  
29 preferred embodiment of my invention, and have described my  
30 invention and the manner and process of making and using it  
31 in such full, clear, concise and exact terms as to enable any  
32 person skilled in the art to which it pertains to make and  
33 use the same, one skilled in the art can easily ascertain the  
34 essential characteristics of this invention and without  
35 departing from the spirit and scope thereof can make various  
36 changes and/or modifications to the invention for adapting it  
37 to various usages and conditions. Accordingly, such changes  
38 and/or modifications are properly intended to be within the  
39 full range of equivalents of the following claims.

## CLAIMS:

1. In a process for producing an ammonia synthesis gas from a methane-containing feedstock gas which includes the steps of reforming the methane-containing feedstock gas in the presence of steam, treating the reformed gas in a shift conversion zone to convert CO catalytically with steam to CO<sub>2</sub> and hydrogen; and removing CO and CO<sub>2</sub> by absorption and methanation from the gas stream withdrawn from the shift conversion zone, the improvement which comprises employing as said feedstock gas a desulfurized, hydrogen-rich gas containing methane and

(a) reforming said hydrogen-rich gas by the steps of:

(i) admixing steam with said hydrogen-rich gas and partially reforming the resulting gas mixture in a tubular heat exchanger containing primary reforming catalyst while maintaining said gaseous mixture in indirect heat exchange with a secondary reformer effluent gas; and

(ii) recovering a partially reformed gas product from said tubular heat exchanger and secondarily reforming said recovered, partially reformed gas product in a secondary reformer in the presence of air, said air being introduced to said secondary reformer in an amount sufficient to provide a hydrogen: nitrogen molar ratio of about 3:1 in the ammonia synthesis gas;

(b) recovering a secondary reformer gas effluent from said secondary reformer and passing said secondary reformer effluent to said tubular heat exchanger for indirect heating of said hydrogen-rich feedstock and steam gas mixture; and

(c) recovering a partially cooled, secondary reformer effluent from said tubular heat exchanger and passing said partially cooled effluent as feed to said shift conversion zone, whereby said ammonia synthesis gas is withdrawn from said methanation step and is suitable for direct feed to an ammonia synthesis reaction.

2. The process of claim 1 wherein said desulfurized, hydrogen-rich feedstock gas contains hydrogen in a concentration of at least about 40 vol.-%.

3. The process of claim 2 wherein said desulfurized hydrogen-rich feedstock gas contains methane in a concentration of from about 10 to 50 vol.-%, calculated on a dry basis.

4. The process of claim 1 wherein said desulfurized hydrogen-rich feedstock gas contains hydrogen in a concentration of from about 50 to about 80 vol.-% and contains methane in a concentration of from about 16 to about 40 vol.-%, calculated on a dry basis.

5. The process of claim 1 wherein said desulfurized hydrogen-rich feedstock gas is obtained by subjecting a hydrogen-rich gas containing COS to hydrolysis in a hydrolysis zone in the presence of steam to form H<sub>2</sub>S from said COS, and removing said H<sub>2</sub>S to form said desulfurized feedstock gas.

6. A process for the production of an ammonia synthesis gas which comprises

(a) forming a mixture comprising steam and desulfurized hydrogen-rich feedstock gas having a temperature of from about 800 to 1200°F;

- (b) passing said steam/feedstock gas mixture to a tubular heat exchanger containing reforming catalyst for partial steam reforming of said feedstock gas, while maintaining said steam/feedstock gas mixture in indirect heat exchange with a secondary reformer effluent gas;
- (c) passing said partially reformed gas mixture and process air, having a temperature of from about 800 to 1200°F, as feeds to said secondary reformer for secondary reforming of said partially reformed feedstock gas;
- (d) withdrawing a gaseous effluent from said secondary reformer and passing said secondary reformer effluent gas to said tubular heat exchanger for said indirect heating of said steam/feedstock gas mixture;
- (e) withdrawing a partially cooled reformer effluent from said tubular heat exchanger and employing said partially cooled reformer effluent to heat additional quantities of said steam/feedstock gas mixture and said process air, thereby forming a further cooled secondary reformer effluent gas having a temperature of from about 1000 to 1200°F;
- (f) passing said further-cooled secondary reformer effluent gas to a shift converter zone wherein shift conversion reactions are effected; and
- (g) recovering an effluent gas from said shift converter zone and treating said shift converter effluent by solvent absorption and methanation to remove CO and CO<sub>2</sub>, to form an ammonia synthesis gas which is suitable as direct feed to an ammonia synthesis reaction.

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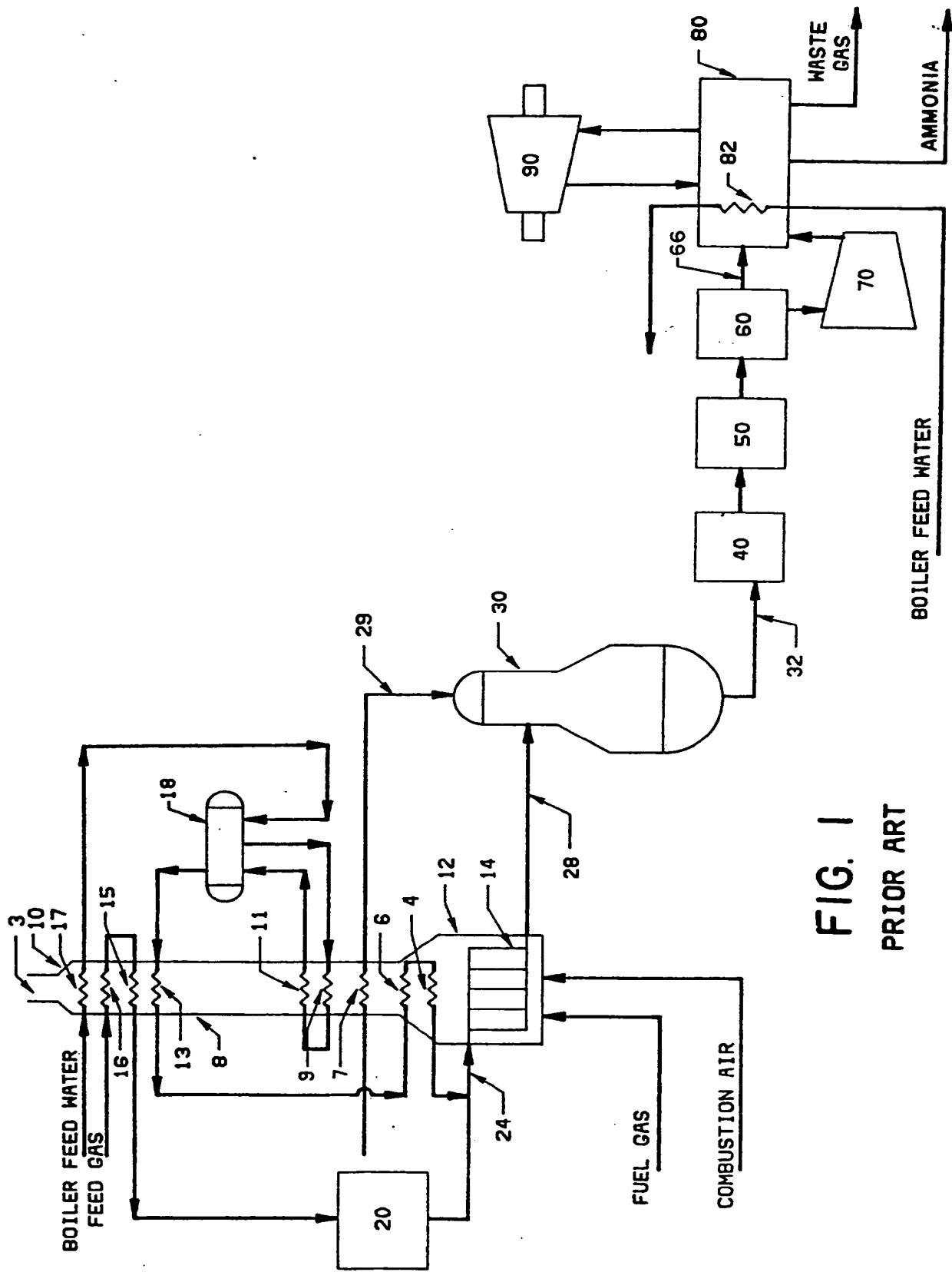
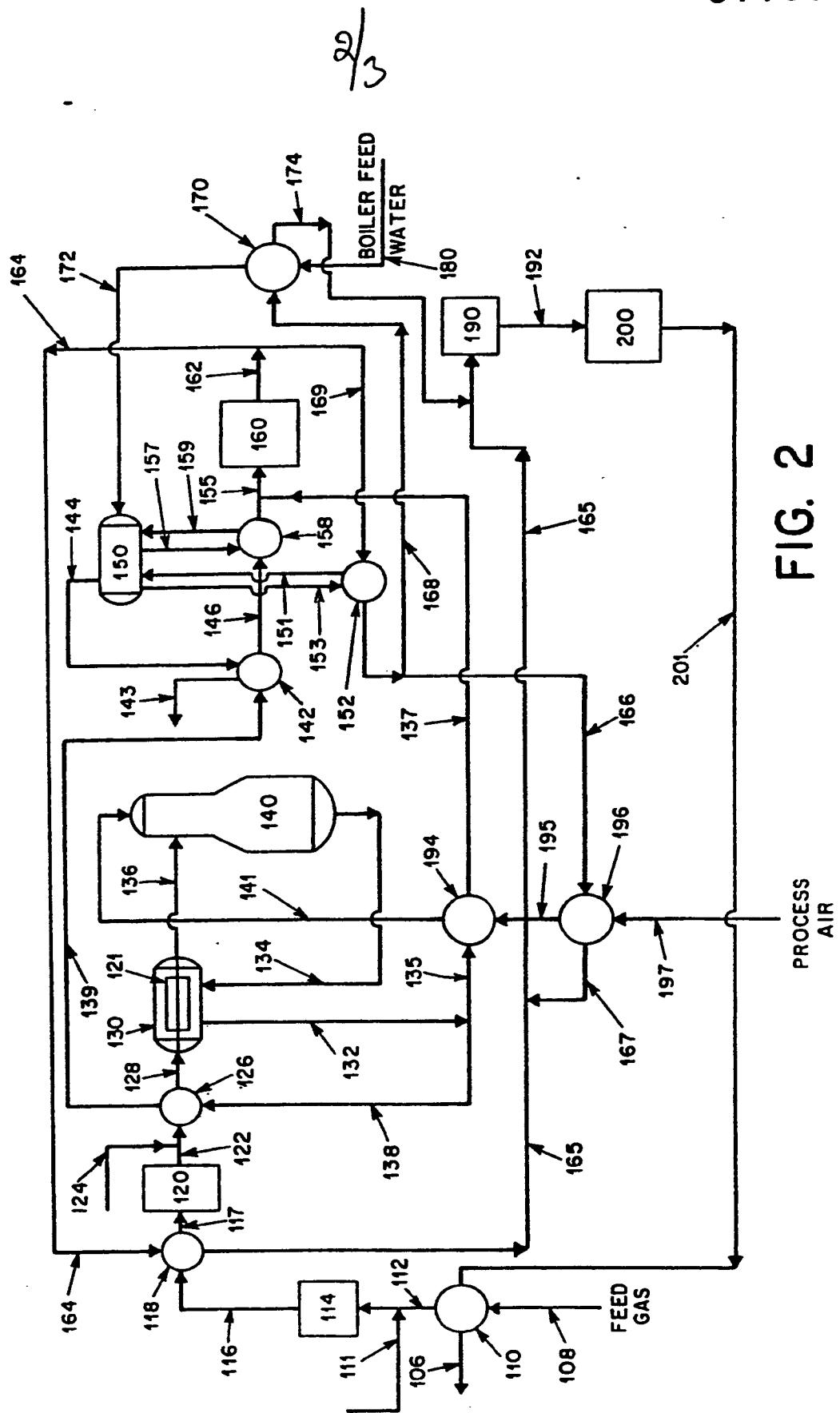


FIG. I  
PRIOR ART



2  
E/G

## PROCESS AIR

3/3

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FIG. 3

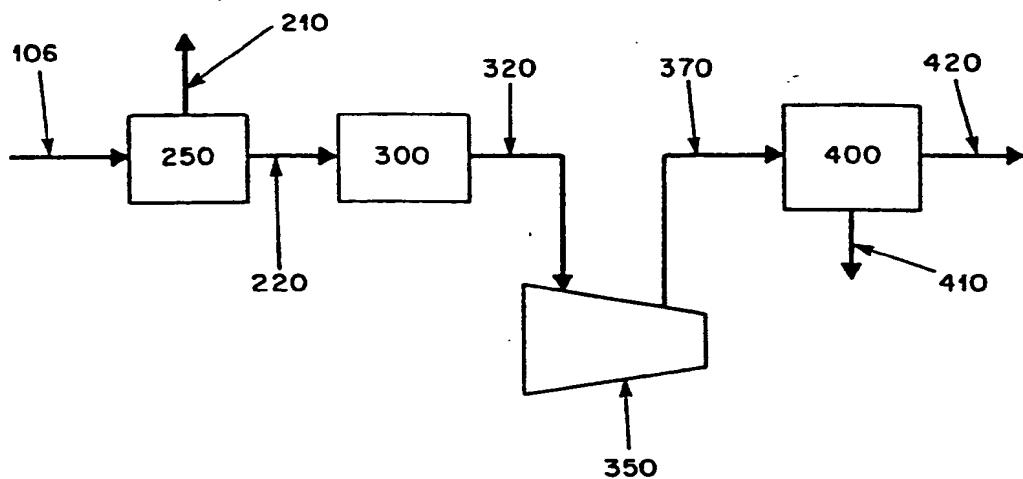
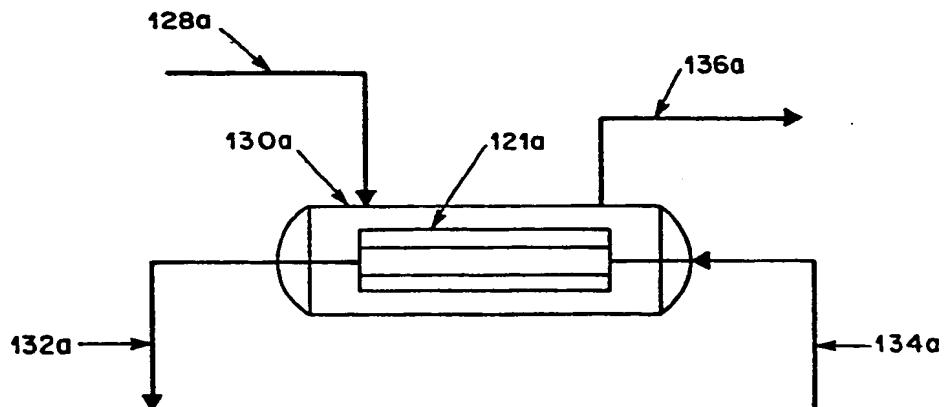


FIG. 4



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⑤ Single-stage reforming of high hydrogen content feeds for production of ammonia syn gas.

⑤ Process for the production of ammonia synthesis gas by steam reforming a desulfurized high-hydrogen-content feedstock gas (122) by admixing steam (124) therewith and partially reforming the resulting gas mixture in a tubular heat exchanger (130) containing primary reforming catalyst while maintaining said gaseous mixture in indirect heat exchange with a secondary reformer effluent gas (134); recovering a partially reformed gas product (136) from the tubular heat exchanger and secondarily reforming this gas in a secondary reformer (140) in the presence of air, which is introduced to the secondary reformer in an amount sufficient to provide a hydrogen: nitrogen molar ratio of about 3 : 1 in the ammonia synthesis gas; and treating the reformed gas (134) in a shift conversion zone (160 + 200) to convert CO catalytically with steam to CO<sub>2</sub> and hydrogen to form a gas which can be treated for removing CO and CO<sub>2</sub> by absorption and methanation to produce the ammonia synthesis gas.

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**EP**



European Patent  
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EUROPEAN SEARCH REPORT

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Application number

EP 83 30 7344

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. *)
X	US-E- 24 311 (MADER) * claim 1 *	1	C 01 B 3/02
A, D	US-A-4 079 017 (CRAWFORD et al.) * claim 1 *	1	
A, D	US-A-3 584 998 (GREEN) * column 2, lines 32-35 *	1	
A	GB-A-2 067 175 (MONTEDEISON S.P.A.) * claim 1 *	1	
	-----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. *)
			C 01 B 3/02
The present search report has been drawn up for all claims			
Place of search BERLIN	Date of completion of the search 02-12-1986	Examiner CLEMENT J. P.	
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>	
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